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COMPLETE SPECIFICATION

Improved Process for producing Town Gas with Low Content of Carbon Monoxide

We, CARLO PADOVANI AND GIULIANO SALVI, both of 15, Via Ampere, Milan, Italy, and ANNUNZIATA FIUMARA, of 14, Via Fucini, Milan, Italy, all Italian citizens, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

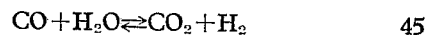
The invention relates to an improved catalytic process of oxidative reforming or oxygenolysis to produce from gaseous or liquid hydrocarbons, in particular from P.F.D. (petroleum flash distillates) a gas of the so-called "town gas" type having a low carbon monoxide content, up to 5%, so as not to be toxic in rooms with normal aeration.

By "oxygenolysis" there is meant here a process of the type also known as "oxidative reforming or conversion" consisting of an almost total gasification of the hydrocarbons which are present in the petroleum distillates by reaction of these distillates with free oxygen (air) or combined oxygen (steam) or with a mixture of said two substances, with generation of gaseous products made up by hydrogen and carbon monoxide, as well as by minor quantities of hydrocarbons, carbon dioxide and nitrogen.

While being rich in hydrogen and quite suitable for replacing common coal gas, the gases produced with this kind of process have the disadvantage of containing a high percentage of carbon monoxide (10—15%), said gas being highly toxic.

Several systems have been suggested to reduce to a minimum the content of said dangerous component. Among these systems those are of particular interest which cause a shift of the so-called homogeneous equilibrium of the water gas to the side which favours

hydrogen generation; i.e. to the right in the following formula:



Said reaction is carried into effect by conducting the gas together with the steam, in excess with respect to the stoichiometric proportions, at temperatures between 300° and 500°C. over catalysts with iron oxide as basic component thereof. 50

The activity of the equilibrium shifting catalysts has a satisfactory life for prolonged periods of time when the process starts from gaseous mixtures of the water-gas type obtained from coke or natural gas or from the so-called condensible oil gases (P.F.D.). Besides having a low sulphur content these gaseous and possibly purified mixtures do not practically contain any hydrocarbons higher than methane. 55

However, if gases obtained from pyrolysis or cracking processes or combined cracking and oxygenolytic processes (such as the so-called distillation gas obtained in gas or in coke plants, or producer gas, or carburetted water gas, or oil gas) are manipulated, then it is required, in order to avoid a rapid deterioration of the catalysts, to submit said gas to cooling, condensation, filtration over active carbon and to washing for eliminating tar vapours, benzol, naphthalene or other polycyclic hydrocarbons, before conducting it to the shifting catalysts. 70

Nevertheless, if the purified gases contain together with oxygen and nitrogen oxides, also gaseous dienic hydrocarbons (although in small quantities) then gums, lacquers or resins may be formed on the catalysts thereby rapidly deteriorating the activity thereof. 75

One of the various attempts to avoid these inconveniences consists in a gas purifi- 80

cation treatment preliminary to the catalytic shifting over catalysts containing copper, molybdenum or sulphides of said two metals.

5 These processes are however quite laborious and require further equipment.

This kind of shifting process generally requires two phases with heat exchangers and possibly with steam addition provided between.

10 All the processes used up to now to produce from liquid hydrocarbons, gases of the common "town gas" type with low carbon monoxide content require a series of distinct and separated operations or processes respectively comprising oxygenolysis, possibly combined with cracking and shifting with intermediate condensation, washing, absorption and possibly a catalytic treatment.

20 These processes require complex and expensive apparatus and are subjected to heat losses which further increase the cost of the produced gas.

To obtain directly from gaseous or liquid hydrocarbons in particular from P.F.D. a gas with a low carbon monoxide content (maximum 5%) which is interchangeable with the common towns gases, the present invention provides a combined pyrolysis, oxygenolysis hydrogenation and catalytic shift-reaction process, characterised in that the hydrocarbons which, from the very beginning, are mixed with all the steam (or air and steam mixture) that is necessary for the successive oxygenolysis and shift-reaction stages are conducted at a temperature of from 600°—1000°C., preferably 650—850°C. over a polyvalent or polyfunctional catalyst adapted to induce the cracking and oxygenolysis as well as an initial shift-reaction, and in that the gas and steam mixture from this first catalytic treatment, after having been cooled to a temperature which is not lower than 350°C. and which, at any rate, is such as not to promote any essential vapour condensation is directly conducted over an hydrogenating catalyst and over a shift-reaction catalyst, wherein heat exchangers are provided between the various stages for supplying the heat necessary to produce and to superheat all the steam necessary for the oxygenolysis, and shift-reactions without any further heat having to be supplied.

55 As clearly disclosed in the course of the following specification, the process according to the present invention permits several other advantages to be achieved, besides the one deriving from the considerable reduction of CO content in the final gases: first of all the possibility of treating gases which have not been previously purified; secondly, the thermal or heat self-sufficiency (leaving out of account, of course, the preliminary heating of the first reactor) and the steam self-sufficiency, whereby the sensible heat of the fluids (flue gases and oxygenolysis gases) from

the oxygenolysing zone, circulating in the several stages, is sufficient for vapourizing the water necessary to produce all the steam required for the various operations as well as to superheat said steam and to satisfy the thermal and chemical demands of the stages following the oxygenolysis stages, the amount of steam initially fed to the oxygenolysis stage being usually sufficient also for meeting the demands of the successive hydrogenation-shifting stages; thus it is made possible to reduce the considerable equipment and operational expenses inherent in the conventional processes for the treatment of cold gases, said expenses deriving from the physical purification, the condensation of the additional steam to be introduced in the shifting phase, and so on.

Other advantages will readily appear to those skilled in the art in the course of the following specification.

According to a preferred embodiment, the process of the invention is performed in a cyclic system as follows.

90 Once the oxygenolysis has been started, endothermic productive steps with gasification of charge hydrocarbons by means of the steam and exothermic heating phases due to the combustion of the charge hydrocarbons with air alternate continuously in the conventional way within a first reactor having placed therein the polyvalent oxygenolysis, pyrolysis and shifting catalyst, the exothermic phases being provided to restore the temperature which had been reduced in view of the endothermic productive reactions as well as to reactivate or revivify the catalyst which had been partially inactivated due to carbon and sulphur compounds.

105 The polyvalent or polyfunctional catalytic mass, upon which the reactions develop, has been the subject of special studies for achieving a contemporaneous oxygenolysis and partial shift-reaction thereof; its composition will be described herein after. A quantity of steam, superheated to 300°—600°C., and hydrocarbons in a ratio of 3:1 to 1.5:1 by weight is conducted over said mass. Besides a partial cracking the catalyst also promotes the oxygenolysis with high conversion efficiency although it operates at temperatures between 650° and 850°C., i.e. at temperatures which are sufficiently low to reduce to a minimum the production of naphthalene and to hold back most of the sulphur which is successively removed with the flue gases. The above mentioned steam-to-hydrocarbon ratio and a 400°—500°C. temperature of the steam introduced in the oxygenolysis zone have been found to be particularly advantageous.

125 As already mentioned, the catalyst used in this first phase is effective to cause a partial shifting, contemporaneously with partial cracking and oxygenolysis, whereby the

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gases flowing from the first reactor, besides having a maximum heat value which is at least 3000 Kcal Nm³ already have a considerably reduced CO content (not larger than 10—12%) and namely such as not to require, normally, a further addition of steam for the shift reaction. The gas and steam mixture flowing from the first reactor is cooled down to lower the temperature thereof from 650°—850°C. to 370°—470°C.

Said reduction is performed in a heat exchange system wherein the sensible heat of these gases is utilized, for instance, for superheating the steam which is to be fed during the oxygenolysis stage. Hence, the gas-steam mixture passes directly, without any intermediate condensation or further steam or heat addition, to the hydrogenation stage over a second catalytic mass suited to facilitate the hydrogenation of the diolefines, of the oxygen and of the nitrogen oxides present in the gases by means of the same hydrogen generated in the first working stage and hence from said stage to the successive shift-reaction stage. Said catalytic mass operates at a temperature of 430°—470°C. and at a space velocity ranging from 4000 to 10,000 Nm³/m³ cat/hr.

Said hydrogenation is sufficient to protect the successive shift-reaction catalyst from possible dangerous or in particular poisonous matters due to oxidation or the production of gums.

Besides the above mentioned system, said temperature reduction may also be effected in other manners; i.e. the gas-steam mixture from the oxygenolysis reactor may be conducted into a waste heat boiler with limited surface.

According to a variant of the process the temperature reduction may be achieved merely by injecting into the gas stream which has been preliminarily purified some atomized water. In this case it is possible to obtain a more precise control of the temperature of the mixture conducted to the shift-reaction stage. The temperature of the second stage (hydrogenation stage) is maintained at between 430°—470°C.; the gaseous purified mixture directly passes from there over a third catalytic mass suited to promote the true shift-reaction at a temperature of 370°—470°C., preferably of 370°—450°C. and at a space velocity ranging from 400 to 1000 Nm³/m³ cat/hr. This shifting operation reduces the CO content to 4—5%. It is possible to reach even lower CO contents (down to 1% and less) by conducting the gases from this first shift-reaction through a heat exchanger which reduces the temperature thereof to 300°—400°C. to a second shift-reaction stage over a catalytic mass similar to the preceding one, which operates at a space velocity ranging from 200—500 Nm³/m³ cat/hr.

Before their outlet, the final gases with reduced CO content transfer their sensible heat in a waste heat boiler to the water that will be transformed into steam which is then superheated, as mentioned, and which is required for the development of the various reactions occurring in the process of the present invention. The autonomous thermal cycle of the process is thus closed in this way. Although other catalytic masses may be used, preferred catalytic masses utilized in the respective phases of the process herein described are:

1) for the oxygenolysis and partial shifting process occurring in the first reactor:

a) a carrier which may be a refractory oxide (such as Al₂O₃, MgO, ZrO₂), a mixture of refractory oxides (such as Al₂O₃—MgO, Al₂O₃—ZrO₂, MgO—ZrO₂, a refractory silicate or a mixture of refractory silicates (Al₂O₃—SiO₂, MgO—SiO₂, Al₂O₃—MgO—SiO₂ or other mixed silicates).

b) an active metal (such as Ni, Fe, and of other metals (such as Cr, Co, Mo) which may be added in variable proportions with a promoting or inducing function and for blocking the binding properties of the support with respect to the active metals.

Said polyvalent or polyfunctional catalyst has already been described in a prior patent (British patent 980,259, Application 34908/60 filed 12th October, 1960).

2) for the hydrogenation operation:

a) a carrier of refractory material (generally of alumina)

b) a mixture of metal oxides with hydrogenating action (such as oxides of Cu, Ni, Co, Mo, Pb)

3) for the final shifting:

a) a mixture of iron oxides (Fe₂O₃, Fe₃O₄)

b) other metal oxides (such as Cr₂O₃) which are added in variable proportions with promoting functions.

In the practical execution of the invention, as shown in Fig. 1 of the accompanying drawings, the mixture of the hydrocarbons, P.F.D. (Petroleum Flash Distillates) to be treated and of the over-heated steam, which is fed through a valve *v* at a temperature of 300—600°C. preferably of 400°—500°C., is introduced through pipe 1 into the first reactor A. Said reactor is also adapted to receive air alternatively introduced therein through the valve *a*. In fact, as previously noted, said continuously operating reactor has productive and heating stages alternatively occurring therein with alternate introduction of steam and air.

The reactor contains a catalytic bed, as already described, whereon the gases react with the steam thus producing a mixture of gas and excess steam which passes, for the purpose of heat exchange, through the super-heater C which also receives from 10

the saturated steam from the waste heat boiler B, super-heated steam from said super-heater C flowing through pipe 4 and valve *v* into the reactor A.

5 The gas-steam mixture which is already in the most favourable ratio for the shifting reaction and at the desired temperature of 370°—470°C. is conducted through pipe 5 directly into the second reactor containing, serially disposed therein, two catalytic beds, i.e. a hydrogenation bed at 430°—470°C. and a shift-reaction bed at 370°—450°C., respectively, wherein the above described reactions of hydrogenation and of shifting at 15 370°—450°C., respectively, take place with a conversion of CO to a content of about 4% in the final gases.

According to a modification of the arrangement just described and illustrated in Fig. 3, an atomizer S adapted to inject a suitably calculated quantity of water into the gaseous mixture may precede the second reactor.

The final gas with a low CO content passes, for a further recovery of its sensible heat, through a pipe 6 into the waste heat boiler where it gives out heat for the vaporization of the water which enters through pipe 9 and leaves at 10 in the form of saturated steam. The gas finally passes 30 to the output or utilization line 7.

As already mentioned, the flue gases from the first reactor are also utilized for the heating of the same boiler which has two sections, said flue gases entering through pipe 3 and leaving through 8 upon having given out their sensible heat.

If in some particular case the CO content in the final gases must be reduced to a value which can be as low as 1% or less then a third reactor F may be provided as shown in Fig. 2, said reactor containing a fourth catalytic bed carrying thereon a catalytic shift-reaction mass similar to the one of the third catalytic bed. In this case the gases from the second reactor pass through 11 first into a heat exchanger E which reduces their temperature from 400°—500°C. to 300°—400°C. and from there through 12 into the reactor F where the further shifting occurs at about 300°—400°C. Finally, the gases from said reactor are conducted through 14 into the waste heat boiler and from there to the discharge.

While the above mentioned embodiments 55 have been described herein by way of example only, it will be understood that different technological processes and conventional equipment may be used as well. In particular the first catalyst may be placed 60 in a reactor of the continuous type (endothermic or thermally neutral) instead of in a reactor of the cyclic type.

The process according to the invention may be applied directly to hydrocarbons or to hydrocarbon mixtures which exhibit a weight ratio C/H lower than or equal to 5.5. If, on the contrary, the weight ratio C/H is higher than 5.5, then it is convenient to reduce said ratio to the above indicated limit before conducting the charge to the oxygenolysis stage. To this aim the feeding charge of the reactor A may be submitted to a mild hydrogenation or, more simply, if it exhibits a sufficiently broad distillation curve it may be fractionated into a head fraction with C/H ratio=5.5 which is conducted to the oxygenolysis and into a tailing fraction which may be used as fuel in the preliminary heating phase of the first reactor A; (the feeding to the oxygenolysis reactor occurs in this case through two distinct ways, one for the heating and the other for production).

The present invention relates to any type of gas to be rendered non-toxic which is obtained with cyclic as well as with continuous processes starting from hydrocarbons for the treatment over three catalysts in series in accordance with the above described teachings.

EXAMPLE I.

A charge made up by light oil distillate P.F.D. having the hereinafter described characteristics is conducted with steam and air alternately into a reactor A containing a first catalytic bed of the above mentioned type, at 700°—800°C., where the oxygenolysis takes place. During the combustion stage the combustion products are conducted for heat exchange to the waste heat boiler B and then to the flue gas outlet or, during the production phase, the production gases leave the reactor A and pass through a steam super heater C of the indirect type in counter-current with respect to the saturated steam; in said steam super heater C the production gases are submitted to a cooling to 370°—470°C. with the assistance, if required, of very finely atomized water injection and they are successively conducted to the second reactor D over the second and then over the third catalytic bed. The converted gas finally gives out its sensible heat in the waste heat boiler and is discharged to the output.

The physical and chemical characteristics of the charge used are as follows in this example:

| | |
|---|--------|
| Specific weight at 15/4°C. | 0.7 |
| Sulphur % by weight | 0.14 |
| Heat value (highest) kcal/kg. | 11.300 |
| Vapour pressure (Reid) at 100°F. p.s.i. | 8 |
| weight ratio C/H | 5.5 |

| | | | |
|---|--|--|---------|
| Distillation: | | II and II catalytic bed (shift-reaction) | |
| Initial point °C. | 42 | Molar ratio steam/CO | 7—9 |
| 50% | 70 | Temperature of the catalytic bed: | |
| 95% | 265 | hydrogenating catalytic layer, | |
| Final point °C. | 288 | °C. | 470°C. |
| Total distillation, % | 97.0 | last catalytic layer; shift- | |
| residue, % | 1.5 | reaction | 450°C. |
| Loss, % | 1.5 | space velocity on the reform- | |
| The operative conditions of the plant re- | | ing gas | 500—800 |
| 10 | lative to the three catalytic masses are as follows: | Table I indicates the characteristics of the | 30 |
| Operational conditions: | | gas obtained in the above referred condi- | |
| I Catalytic bed (Oxygenolysis) | | tions; at the side is shown by way of com- | |
| Molar ratio steam P.F.D. | 15—20 | parison the composition of the gas examined | |
| 15 | Temperature of the catalytic bed | after the first catalytic layer namely the gas | |
| | min-max | from the oxygenolysis (without the conversion | 35 |
| | | of CO into CO ₂). | |
| | Initial part of the catalytic bed, | | |
| | 750—800°C. | | |
| | Centre of the catalytic bed, | | |
| | 700—750°C. | | |
| 20 | End of the catalytic bed, | | |
| | 690—730°C. | | |

TABLE I

| Composition | After the three catalytic layers | After the first catalytic layer |
|---|-------------------------------------|------------------------------------|
| | with conversion | without conversion |
| CO ₂ , % by volume | 18.3 | 13.0 |
| CnHm , % „ „ | | 9.8 |
| O ₂ , % „ „ | 0.4 | 0.3 |
| CO , % „ „ | 3.7 | 11.2 |
| H ₂ , % „ „ | 52.3 | 50.0 |
| CH ₄ , % „ „ | 9.9 | 8.8 |
| C ₂ H ₆ , % „ „ | 2.0 | 1.4 |
| N ₂ , % „ „ | 5.9 | 5.5 |
| Heat value (highest), Kcal/m ³ | 4500. | 4700. |
| Relative density | 0.59 | 0.58 |
| Wobbe index | 5920. | 6180. |

EXAMPLE II.

- 40 This example relates to the process described in the diagrammatic representation shown in Fig. 2; the charge exhibiting the characteristics which have already been shown in the example 1 is conducted to the reactor A alternately with steam and with air.
- 45 The gases obtained during the production phases pass through the super heater C in
- countercurrent with respect to the steam from the heat exchanger E and are then conducted to the second reactor D containing the second and the third catalytic bed. The converted gas passes then through the exchanger E (in countercurrent with respect to the steam from the boiler B) where it is submitted to a partial cooling from 450°—500°C. to 350°—400°C. and is then conducted to a third re-
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- 55

- actor where the last stage of the shift-reaction occurs. The final gas gives out its sensible heat in the waste heat boiler B before being conducted to the output.
- 5 The operative conditions of the reactors A and B correspond to the ones indicated in the first example; the operative conditions of the third reactor (4th catalytic bed) are as follows:
- 10 Molar ratio steam/CO 17—23
Temperature of catalytic bed 350°—380°C.
Space velocity of the gases fed to the reactor Nm³/m³ catalyst/hour 200—500
- 15 The characteristics of the gas produced in the above indicated conditions are shown in the following:
- Composition:
- | | | | |
|---------------------------------------|-------------|-------|----|
| CO ₂ | % by volume | 19.8% | 20 |
| CnHm, | % " " | 7.4% | |
| O ₂ , | % " " | 0.4% | |
| CO, | % " " | 0.8% | 25 |
| H ₂ , | % " " | 54.2% | |
| CH ₄ , | % " " | 9.6% | |
| C ₂ H ₆ , | % " " | 2.0% | |
| N ₂ , | % " " | 5.8% | |
| Higher heat value kcal/m ³ | | 4450. | 30 |
| Relative density | | 0.60 | |
| Wobbe index | | 5779. | |
- EXAMPLE III
- The hydrocarbons charge to be treated exhibits a weight ratio C/H=5.6. It is therefore convenient to submit said hydrocarbons to a distillation fractioning into a head fraction with weight ratio C/H=5.4 and into a tailing fraction with ratio C/H=6.0 the composition of which is indicated in the following table:

| Characteristics | Material as it is | Head Fraction | Tailing Fraction |
|--|-------------------|---------------|------------------|
| Specific weight at 15/4° C. | 0.720 | 0.685 | 0.800 |
| Sulphur, % by weight | 0.15 | 0.10 | 0.26 |
| Heat value, kcal/Kg. | 11.250 | 11.350 | 11.100 |
| Vapour pressure (Reid) at 100° F. p.s.i. | 7. | 8. | 5. |
| Weight ratio C/H | 5.6 | 5.4 | 6.0 |
| Distillation: | | | |
| Initial point °C. | 45 | 45 | 75 |
| 30% by volume distillates at °C. | 70 | 52 | 120 |
| 50% " " " " " | 85 | 60 | 150 |
| 70% " " " " " | 130 | 90 | 190 |
| 90% " " " " " | 240 | 130 | 250 |
| Final point °C. | 300 | 150 | 335 |

- 40 The head fraction may be submitted successively to the treatment described in example 1 while the tailing fraction is utilized in the same reactor during the heating phases.
- WHAT WE CLAIM IS:—
- 45 1. Process for producing town gas or the like with very low carbon monoxide content (not larger than 5% by volume) which is interchangeable with the common town or coal gas, by means of a combined pyrolysis or cracking, oxygenolysis, hydrogenating and
- shift-reaction process, characterised in that the gaseous or liquid hydrocarbons in particular P.F.D. which have been previously mixed with all the steam (or air-and-steam mixture) that is necessary for the successive oxygenolysis and shift-reaction stages are conducted, at a temperature from 600°—1000°C., over a polyvalent catalyst adapted to induce partial cracking of the hydrocarbons, oxidation (oxygenolysis) of the latter with steam as well as an initial shift-reaction of the carbon

monoxide produced, and in that the gas-steam mixture from this first catalytic treatment, upon having been cooled in counter current with steam coming from a waste heat boiler to a temperature which is not lower than 350°C., is next conducted over an hydrogenating catalyst and over a shift-reaction catalyst, wherein heat exchangers are provided between the various stages for supplying the heat required to produce and to superheat all the steam necessary for the oxygenolysis and shift-reaction without any further heat having to be supplied, the operative conditions being so adjusted that the final gas has a heat value which is not lower than 3000 Kcal/Nm³ and such combustion characteristics as to make it interchangeable with the common town gas.

2. The process according to claim 1, characterised in that the sensible heat of the gases circulating from the oxygenolysis stage to the outlet of the final gas is sufficient to meet the heat demand of the shift-reaction stage, and in that all the steam necessary for the development of the various stages of the process is initially added with the feeding to the oxygenolysis stage in the weight ratio "steam-to-hydrocarbons" comprised between 1.5 to 1 and 3 to 1.

3. The process according to the preceding claims, characterised in that the quantity of superheated steam initially added to the hydrocarbons fed in the oxygenolysis zone in a ratio up to about 3:1 is sufficient also for the reactions occurring in the hydrogenation and shift-reaction zones.

4. The process according to any of the preceding claims, characterised in that the steam which must react with the hydrocarbons in the oxygenolysis zone is superheated to a temperature ranging between 300° and 600°C.

5. The process according to any of the preceding claims, characterised in that the catalyst used in the first phase is polyvalent or polyfunctional so as to be adapted to promote a partial cracking of the hydrocarbons, an oxygenolysis of the hydrocarbons with steam and also a partial shifting of the homogeneous equilibrium of the water gas, said catalyst being essentially constituted of a carrier having as basic component a refractory oxide such as aluminium oxide, magnesium oxide, zirconium oxide or mixtures thereof, or a refractory silicate such as aluminium silicate, zirconium silicate or mixtures thereof, or an active metal such as Ni, Fe or other metals (such as Cr, Co, Mo) having a substantial promoting function or being adapted to block the binding properties of the support with respect to the active metals.

6. The process according to any of the preceding claims, characterised in that the polyvalent cracking, oxygenolysis, and shift-reaction catalyst of the first phase is active

within a temperature range preferably of from 650° to 850°C.

7. The process according to any of the preceding claims, characterised in that the catalyst used for the hydrogenation is constituted by a carrier of refractory material preferably of alumina and by a mixture of metal oxides with hydrogenating action (such as Co, Ni, Mo, Cu, Pb) and operates at a temperature of 430°—470° and at a space velocity ranging from 4,000 and 10,000 Nm³/m³ cat/hr.

8. The process according to any of the preceding claims, characterised in that the catalyst used for the shift-reaction is constituted by a mixture of iron oxides (Fe₂O₃, Fe₃O₄) and by other metal oxides such as chromium oxide Cr₂O₃ which are added in variable proportions with promoting function, and operates at a temperature ranging between 370°—470°C., preferably of 370°—450°C. and at a space velocity ranging from 400 and 1000 Nm³/m³ cat/hr.

9. The process according to any of the preceding claims, characterised in that the steam necessary for the various reactions is produced by utilising the sensible waste heat of the flue gases flowing from the oxygenolysis heating zone as well as the heat of the final gases.

10. The process according to any of the preceding claims, characterised in that the gases flowing from the oxygenolysis zone, before passing to the hydrogenating-shift-reaction zone, are conducted through a heat exchange zone wherein their temperature is reduced from 650°—850°C. to 370°—470°C. their sensible heat being utilised for superheating saturated steam from the waste heat boiler to be fed to the oxygenolysis zone.

11. The process according to claim 10, characterised in that the gases flowing from the oxygenolysis and/or heat exchange zone are submitted to a cooling which is controlled by means of injection of atomised water.

12. The process according to any of the preceding claims, characterised in that the mixture of gas and excess super-heated steam flowing from the first catalytic zone already has the correct composition for being introduced into the shift-reaction zone.

13. The process according to any of the preceding claims, characterised in that the gases flowing from the shift-reaction zone successive to the oxygenolysis zone are conducted to an additional shift-reaction zone over catalysts which are similar to those of the first shift-reaction zone, at a temperature between 300°—400°C. and at a space velocity comprised between 200 and 500 Nm³/m³ cat/hr., so as to obtain a final gas which has a carbon monoxide content which can be as low as 1% or less.

14. The process according to claim 13, characterised in that the first and the second shift-reaction zone comprise a zone of cooling to 300°—400°C. intermediately disposed therebetween, said cooling zone serving for heat exchange between the gases from the first shift-reaction zone and saturated steam from the waste heat boiler.

15. A process for producing town gas or the like with low carbon monoxide content from hydrocarbon material, wherein the hydrocarbon material is subjected to a preliminary hydrogenation treatment so as to reduce the weight ratio C/H thereof to 5.5 or less, and is subsequently submitted to a process in accordance with the claims 1—12 or 13 and 14.

16. The process for producing town gas or the like with low carbon monoxide content from hydrocarbon material having a weight ratio C/H higher than 5.5, characterised in that said hydrocarbon material is subjected to fractionation to produce a head fraction having a ratio C/H equal to or lower than 5.5 which is conducted to the oxygenolysis according to the process claimed in Claims 1—12 or 13 and 14, and a tailing fraction having a ratio C/H higher than 5.5 which is utilised as fuel in the heating phase of the oxygenolysis zone.

17. Apparatus for carrying into effect the process according to claims 1—12, characterised in that it comprises a first cyclic reactor provided with pipes for the feeding of air and of superheated steam through input and output valves and with pipes for the feeding of hydrocarbons to be treated, said reactor containing a catalytic bed suited to promote said cracking, oxygenolysis and partial shift-reactions as well as heating reactions according to whether superheated steam or oxygen (air) are respectively fed to said reactor, a steam superheater, in which saturated steam flowing from a boiler and directed to the oxygenolysis reactor is superheated with the sensible heat of the gases produced in the reactor until the temperature of these latter gases is lowered from 650—850°C. at the inlet to 430—470°C. at the outlet, a second reactor suited to operate also with oxygenolysis gases obtained with continuous endothermic or autothermic (instead of cyclic) plants, said reactor containing two catalytic beds disposed in series, the first one being an hydrogenating bed at 430—470°C., the second one being a shift-reaction bed at 370—450°C., said two beds being successively traversed by the production gases flowing from the superheater, and a waste heat boiler which is constituted of two sections and

is heated by the sensible heat of the flue gases from the oxygenolysis reactor and of the final gases with low carbon monoxide content flowing to the output, the saturated steam which is to be superheated in said superheater before passing to the oxygenolysis reactor being produced in said waste heat boiler.

18. Apparatus according to claim 17, characterised in that the second reactor is followed by a third reactor containing a fourth catalytic bed adapted to effect a further shift-reaction on the gases from the second reactor until the final production gases contain a percentage of carbon monoxide which can be as low as 1% or less.

19. Apparatus according to claim 18, characterised in that a heat exchanger is provided between the second and the third reactor, said heat exchanger being adapted to reduce the temperature of the gases from the second reactor from 400—500°C. flowing to 300—400°C. while at the same time heating saturated steam from the boiler directed to the superheater.

20. Apparatus according to claim 17, characterised in that it further comprises an hydrogenation plant for the hydrocarbons to be treated, said plant being mounted before the oxygenolysis reactor in order to reduce the weight ratio C/H to 5.5 or less, the head products of said plant being conducted to said oxygenolysis reactor while the tailing products are utilised for the heating of said reactor.

21. Apparatus according to claim 17, characterised in that it further comprises a plant for fractionating the hydrocarbons to be treated, said fractionating plant being mounted before the oxygenolysis reactor, the head products of said fractionating plant being conducted to said oxygenolysis reactor and the tailing products being utilised for the heating of said reactor.

22. Town gas or the like with a carbon monoxide content which is not larger than 5%, said gases being obtained according to the process and the apparatus described in one or more of the preceding claims.

23. Town gases or the like having a carbon monoxide content as low as 1% or less, said gases being obtained according to claim 13 and in the apparatus of claims 18 or 19.

24. Town gas production according to claim 1, substantially as herein described and illustrated in the accompanying drawings.

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